Synopsis

Synopsis of the thesis entitled "Electrocatalytic Studies on Layer-type Ternary Phosphochalcogenides and on the Formation of Nitride Phases" submitted by Mr. Sujoy Sarkar under the supervision of Prof. S. Sampath at the Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore-560012, India, for the Ph.D. degree in the Faculty of Science.

Research on new, environment-friendly, clean and efficient energy sources have contributed immensely to the development of new technologies for the generation and storage of electrical energy. Heterogeneous 'electrocatalysis' involves catalysis of redox reactions where the electrode material, termed as 'electrocatalyst' reduces the overpotential and maximizes the current for the processes occurring at the electrode/electrolyte interface. Efficient catalysts for hydrogen evolution reaction (HER), oxygen evolution reaction (OER), and oxygen reduction reaction (ORR) are of paramount importance for electrochemical energy generation and storage applications in water splitting, fuel cells and batteries. However, high cost of Pt catalysts that are commonly used for such applications restricts their commercial viability. In addition, there are issues related to poisoning of the surface under certain conditions. One particular case of direct methanol fuel cells involves problems of methanol tolerance as well. Hence, the on-going search in this direction, is to search for alternate catalysts that can match the performance of Pt. There is a quest for the development of stable and durable electrocatalysts/ supports for various electrochemical redox reactions particualrly based on energy storage and conversion.

The present thesis is structured in exploring the multi-functional aspects of ternary palladium phosphochalcogenides (PdPS and PdPSe) that possess layer-type structure with high crystallinity. They are semiconducting in nature and possess favorable electrochemical, electrical and optical properties. The chalcogenide compounds crystallize in orthorhombic symmetry with an indirect band gap close to 1.5 eV. The current study shows the versatility of ternary phosphochalcogenides in the bulk phase as well as in small sizes. The electrocatalytic activities of the chalcoenides are found to be dramatically improved by increasing the electrical conductivity by way of forming composites with reduced graphene oxide (rGO). The average crystallite size of the PdPS and PdPSe are 30 μm ±10 μm (figure 1). The composites are prepared by simple

hydrothermal methods without use of any reducing agent and are characterized using various physico-chemical techniques.

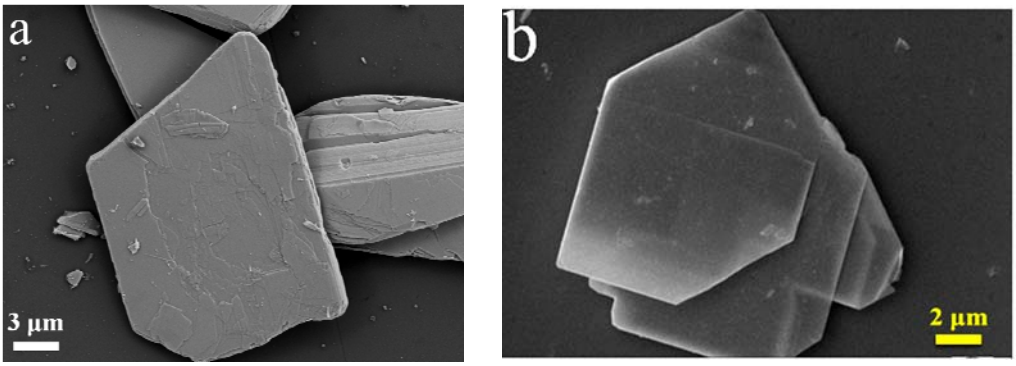

Figure 1. FESEM images of (a) PdPSe and (b) PdPS.

In the present investigations, PdPS and its reduced graphene oxide composite (rGO-PdPS) are shown to be very efficient hydrogen evolution electrocatalysts (figure 2a). The bulk form of PdPS is found to be very active and the composite of PdPS with reduced graphene oxide improves the hydrogen evolution performance dramatically, even superior to state of the art, MoS_2-based catalysts.

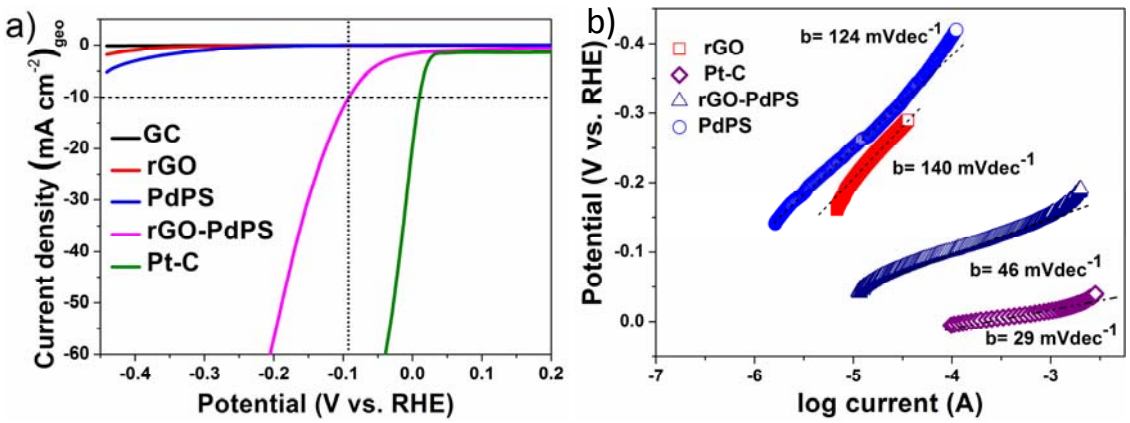

Figure 2. (a) Linear sweep voltammograms of rGO, bulk PdPS, rGO-PdPS composite and 40 % Pt-C in 0.5 M H_2SO_4 solution (pH 0.8). Scan rate used is 1 mV s^{-1}. (b) Tafel plots for PdPS, rGO, rGO-PdPS and 40 wt% Pt-C in 0.5 M H_2SO_4 at 1 mVs^{-1} scan rate.

The Tafel slope and the exchange current density values associated with hydrogen evolution reaction are 46 mV dec^{-1} and 1.4 x 10^{-4} A cm^{-2} respectively (figure 2b). The stability of the PdPS-based catalyst is found to be excellent retaining same current densities even after thousand cycles. Moreover, post-HER characterization reveals the

durability of the material even after cycling for a long time. Preliminary spectroelectrochemical investigations are attempted to gain further insight in to the HER.

Subsequently, the PdPS and its composite are explored as ORR catalysts in alkaline medium. The composite of PdPS with rGO is formed to enhance the catalytic activity of pure PdPS and the electron transfer kinetics is found to be very favorable. The kinetics of the oxygen reduction reactions are followed by RDE/RRDE measurements. It is experimentally verified that the composite eletrocatalyst is very stable, efficient and methanol tolerant in alkaline medium. The characteristics of the composite catalyst are comparable with widely used standard Pt-C for ORR (figure 3a). Moreover, ternary phophochalcogenide, PdPS, combined with rGO shows good catalytic activity towards OER and it affords a current density of 10 mA cm^{-2} at an overpotential of η = 570 mV (figure 3b).

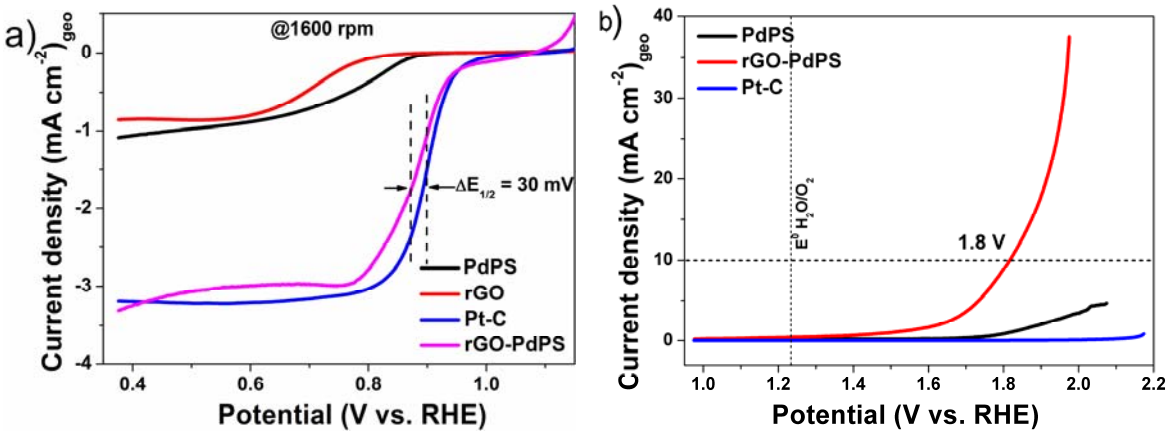

Figure 3. (a) Comparative voltammograms for rGO, bulk PdPS, rGO-PdPS and 40 % Pt-C in 1M KOH at 1600 rpm. The potential is swept at a rate of 5 mVs^{-1}. (b) Linear sweep voltammograms of oxygen evolution reaction on rGO-PdPS, PdPS and 40 % Pt-C in 1 M KOH electrolyte. Scan rate 5 mV s^{-1}.

Apart from its tri-functional electrocatalytic behavior, PdPS and its rGO composite act as an anode material for Li-ion batteries showing high storage capacity of lithium (figure 4). The capacity fading of bulk PdPS is analyzed using XRD and SEM. The introduction of rGO, a well-known conducting matrix, improves the performance.

Palladium phosphorous selenide (PdPSe) and its composite with rGO (rGO-PdPSe) are also explored as electrocatalysts for HER, ORR and OER. They show the tri-functional electrocatalytic behavior as well.

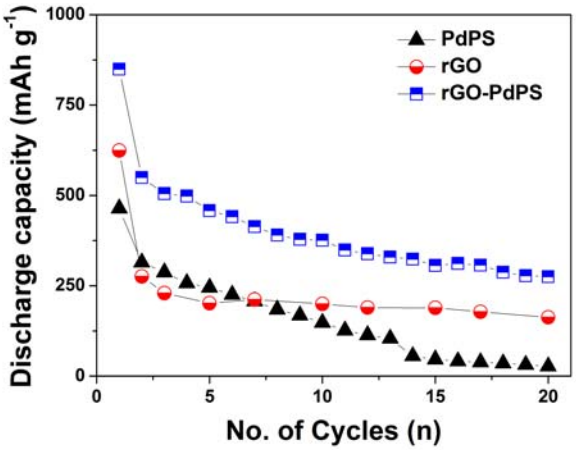

Figure 4. Discharge capacity as a function of number of cycles for PdPS, rGO rGO-PdPS electrode at current density of 35 mAg^{-1} in rechargeable lithium ion battery.

The next chapter deals with single or few layer PdPS where layer-type PdPS is exfoliated by several methods such as ultra-sonication and solvent exfoliation. Various microscopic and spectroscopic techniques have been used to characterize the material. These sheets show significantly improved electrocatalytic activity towards ORR and HER with notably low onset potential and low Tafel slopes. The charge storage capacity also increases by an order from its bulk counterpart. The catalyst shows excellent stability for HER and good methanol tolerance behavior towards ORR is also observed. This opens up possibilities for applications of few-layer ternary phosphosulphides in energy conversion and storage. However, one should be cautious since the exfoliation results in a slightly different composition of the material.

Different aspects of electrodeposition of gallium nanoparticles on exfoliated graphite surfaces from aqueous acidic solution forms part of the next study. The electrodeposited surface is characterized by various microscopic and spectroscopic techniques. The presence of surface plasmon peak in the visible region has led us to explore the use of Ga on EG for SERS studies. This preliminary work shows that the Raman signal of R6G is enhanced in the presence of Ga deposited on EG surface.

The research work presented in the next part of the thesis deals with the preparation, physicochemical, spectroscopic characterization of room temperature molten electrolytes based on amides. Room temperature ternary molten electrolyte involving a combination of acetamide, urea and gallium nitrate salt is prepared and the molten eutectic is characterized. An electrochemical process is developed for depositing gallium nitride from the ternary molten electrolyte on Au electrode. Gallium ion is reduced at low

potentials while nitrate ion is reduced to produce atomic nitrogen, forming gallium nitride under certain conditions. Au coated TEM grid is used for patterning gallium nitride (figure 5). The deposited gallium nitride is further annealed at high temperature to increase the crystalinity and improve the stoichiometry of gallium nitride.

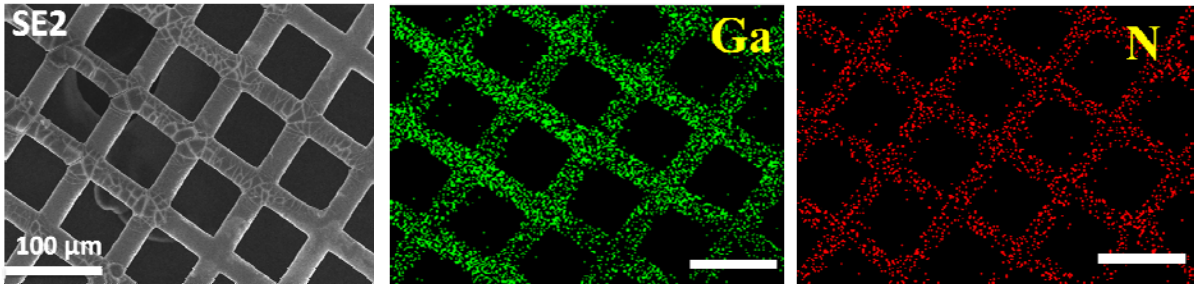

Figure 5. The FESEM image of patterned gallium nitride deposited on Au coated TEM grid. Elemental mapping of Ga and N from the same region is given.

The last chapter explores the prepration and uses of textured GaN tubes synthesized from GaOOH rod-like morphology. The precursor material is prepared by simple hydrothermal technique, maintaining certain value for the pH of the solution. The thermal treatment under ammonia atmosphere leads to highly crystalline, single phase textured tube- like morphology. The as-prepared material is explored as photoanodes in photoelectrochemical water splitting, dye sensitized solar cells and active substrate for SERS. The appendix-I discusses the Na-ion storage capacity by rGO-PdPS composite whereas appendix-II deals with the synthesis of InN and FeN from ternary molten electrolyte.